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EXAMINATION OF LEACH RESIDUES FROM THE ZINC PLANT OF KIDD CREEK MINES LIMITED, TIMMINS, ONTARIO

by

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ABSTRACT

Leaching operations at the zinc plant of Kidd Creek Mines Limited, Timmins, Ontario currently produce both a neutral leach residue and a high acid leach residue. Jarosite-type compounds were found in both residues in major and minor amounts. X-ray diffraction analysis revealed dominant lead jarosite together with lesser amounts of a phase resembling sodium jarosite. SEM-EDX studies confirmed the presence of fine-grained jarosite-type compounds, but could not distinguish separate lead and alkali jarosite phases. This suggests that the two types of jarosite are intimately mixed, and possibly occur in zoned crystals. Silver was consistently associated with the jarosite phase, and likely substitutes for lead and the alkalis in the jarosite structure.

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ÉTUDE DES RÉSIDUS DE LESSIVAGE PROVENANT DE L'USINE DE ZINC DE LA KIDD CREEK MINES LIMITED, À TIMMINS (ONTARIO)

Par J.E. Dutrizak*, T.T. Chen* et J.L. Jambor*

RÉSUMÉ

Les opérations de lessivage à l'usine de zinc de la Kidd Creek Mines Limited, à Timmins, en Ontario, produisent actuellement un résidu neutre et un résidu fortement acide. Des composés de type jarosite sont présents dans les deux types de résidus en quantités élevées et faibles. La diffractométrie révèle la présence d'une quantité importante de jarosite plombifère et d'une quantité plus faible d'une phase ressemblant à la jarosite sodique. Les études au microscope électronique à balayage et par diffraction électronique des rayons X confirment la présence de composés fins de type Jarosite, mais ne permettent pas de distinguer les phases de jarosite plombifère et alcaline. Il semble donc que les deux types de jarosite sont intimement mêlés et qu'ils pourraient se présenter dans des cristaux zonés. L'argent est toujours associé à la phase de jarosite et remplace probablement le plomb et les alcalis dans la structure de la jarosite.

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INTRODUCTION

As part of its Silver Recovery in the Zinc Industry Project, CANMET has been carrying out a detailed mineralogical-chemical balance of the zinc plant of Kidd Creek Mines Limited, Timmins, Ontario. Recently, operations at that plant were altered from a one-residue process to a two-residue process (Figure 1) to try to recover more of the silver from the zinc concentrates. Following completion of the plant modifications, ten samples of leach residue were provided for study. These consisted of five samples of unwashed neutral leach residue (#3 thickener underflow) and five samples of unwashed high acid leach residue (#1 thickener underflow). The five samples were designated as follows.

Neutral Leach Residue	High Acid Leach Residue
#8260	#8265
#8288	#8293
#8294	#8298
#8300	#8304
#8305	#8309

For the purpose of the investigation, it was considered necessary to ascertain: 1) if lead jarosite is present, 2) if more than one jarosite species occurs and 3) how the silver is present in the residues. These questions as well as a general characterization of the residues are answered in this brief report.

EXPERIMENTAL

The as-received samples were slurried with water at ~40°C, filtered and then washed with 3 to 4 L of H_2O to remove soluble salts. The washed residues were dried at 110°C prior to bulk chemical analysis by conventional methods.

The washed residues were examined by a combination of 114.6 mm Debye-Scherrer and Guinier X-ray powder diffraction methods both to identify the principal phases and to differentiate the jarosite-type compounds, all of which have similar powder diffraction patterns.

Some of the residues were washed with 10% ammonium acetate solution (1) to remove free $PbSO_4$. Other residues were cyclosized to try to eliminate coarse gangue and ferrite particles from the generally fine-grained jarosite phases. Polished sections of the various residues were prepared and examined using conventional light microscopy as well as scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX). Although most of the jarosite-type particles were <10 μm, these were also examined with a MAC 400 electron microprobe to try to detect silver. Because the beam invariably overlapped the mounting material, however, low total analyses were usually obtained and the method yielded only semi-quantitative results.

RESULTS AND DISCUSSION

The chemical analyses of the washed neutral leach and high acid leach residues are given in Table 1, and the corresponding X-ray powder diffraction data are presented in Table 2.

Chemically, all the neutral leach residues are fairly similar in that they contain low levels of alkalis (except #8294) and modest concentrations of silver and lead. There is more than adequate Fe and SO_4 to form jarosite-

Table 1 - Chemical Analyses of the Kidd Creek Zinc Plant Residues

	Na(%)	K(%)	Ag(ppm)	Pb(%)	Fe(%)	SO_4(%)*
Neutral Leach Residues						
#8260	0.19	0.09	255	1.35	33.42	6.53
#8288	0.19	0.09	313	1.63	34.01	6.74
#8294	0.62	0.09	265	1.52	32.66	10.58
#8300	0.15	0.09	255	1.58	34.23	6.80
#8305	0.12	0.07	266	1.57	33.86	5.93
High Acid Leach Residues						
#8265	0.79	0.51	1400	10.67	19.67	23.84
#8293	0.78	0.56	1190	10.61	20.70	21.30
#8298	1.20	0.42	747	8.20	24.92	22.52
#8304	1.25	0.49	931	6.97	20.34	22.88
#8309	0.95	0.63	1039	6.83	21.28	22.97

* Total sulphur expressed as SO_4

Table 2 - X-ray Powder Diffraction Analyses of the Kidd Creek Zinc Plant Residues

Neutral Leach Residues	Phases Present
#8260	zinc ferrite, trace jarosite-type
#8288	zinc ferrite, minor jarosite-type
#8294	zinc ferrite, minor jarosite-type
#8300	zinc ferrite, minor jarosite-type
#8305	zinc ferrite, minor jarosite type
High Acid Leach Residues	
#8265	zinc ferrite, $PbSO_4$, major jarosite-type, trace SnO_2
#8293	zinc ferrite, $PbSO_4$, major jarosite-type, trace quartz, SnO_2
#8298	zinc ferrite, $PbSO_4$, major jarosite-type, trace quartz, SnO_2
#8304	zinc ferrite, $PbSO_4$, major jarosite-type, trace quartz, SnO_2
#8309	zinc ferrite, $PbSO_4$, major jarosite-type, trace quartz, SnO_2

type compounds with the alkalis, silver and lead present. All the high acid leach residues are also fairly similar and are distinguished from the neutral leach residues by their moderately high concentrations of Na and K and by their major lead and silver concentrations. Again there is adequate Fe and SO_4 to react with all the Na, K, Ag and Pb to form jarosite-type compounds.

X-ray diffraction analysis (Table 2) showed the neutral leach residues to be generally similar in that they consist predominantly of zinc ferrite together with trace or minor amounts of jarosite-type compounds. Careful study of the X-ray powder diffraction patterns revealed that many of the jarosite lines are split, suggesting the presence of two jarosite species. The main species in all the samples seems to be lead jarosite; the films are in good agreement with synthetic Pb-H_3O (disordered) jarosites. The other jarosite in the sample is similar to sodium jarosite, but identification of some of the members within the jarosite group by X-ray diffraction alone is uncertain. Based on the relative intensities of their 0.0.12 lines, the estimated ratio of lead jarosite to sodium jarosite in #8294 is 4:3.

In the high acid leach residue, X-ray diffraction analysis indicated the presence of major zinc ferrite, $PbSO_4$ and jarosite-type compounds together with traces of quartz. Again there is an indication of two jarosite-type compounds, likely lead jarosite and sodium jarosite. Based on the intensities of their 0.0.12 lines, the estimated ratios of lead jarosite to sodium jarosite are as follows.

Sample	Pb jarosite:Na jarosite
#8265	2:1
#8298	1:1
#8309	4:1

Possibly there has been an increase in the ratio of lead jarosite to sodium jarosite during the high acid leaching stage.

One sample each of the neutral leach residue (#8294) and high acid leach residue (#8298) was leached in cold, 10% ammonium acetate solution to extract $PbSO_4$; this procedure does not affect lead jarosite (1). The analytical data are summarized in Table 3.

Table 3 - Chemical Analysis of the Residues Before and After Ammonium Acetate Leaching

Element	Neutral Leach Residue		High Acid Leach Residue	
	Before	After	Before	After
Na	0.62	0.65	1.20	1.16
K	0.09	0.10	0.42	0.27
Ag	265	298	747	798
Pb	1.52	1.81	8.20	5.72
Fe	32.66	34.63	24.92	27.30
SO_4*	10.58	9.29	22.52	20.70

The neutral leach residue has hardly been affected, suggesting that virtually all the lead is present as lead jarosite. There is a significant drop in the lead and sulphate contents of the high acid leach residue after ammonium acetate leaching, in agreement with the presence of $PbSO_4$ in this material. Even in the high acid leach residue, however, lead jarosite seems to be the dominant lead carrier as based on the residual lead analysis and the absence of $PbSO_4$ lines in the powder diffraction

* Total sulphur expressed as SO_4

patterns of the acetate leached residues. Both lead jarosite and sodium jarosite (?) were identified in the ammonium acetate-leached residues, and the relative amounts of the two species were almost the same as before leaching.

Preliminary microscopic study of the as-received high acid leach residue showed the jarosite-type phases to be very fine grained. Accordingly, this residue was cyclosized to try to eliminate zinc ferrite, $PbSO_4$ and quartz and to concentrate the jarosites for further study. The chemical analysis of the -10 μm fraction is given in Table 4.

Table 4 - Chemical Analysis of the As-received and Minus 10 μm Fraction of High Acid Leach Residue (#8298)

Element	As-Received	-10 μm
Na	1.20	1.69
K	0.42	0.43
Ag	747	918
Pb	8.20	8.70
Fe	24.92	23.93
SO_4*	22.52	25.32

The -10 μm fraction appears to have been only slightly enriched in jarosite-type species as reflected by the alkali and lead contents. Silver is also concentrated in the finer fractions.

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* Total sulphur expressed as SO_4

Figure 2 shows the general field of view of the -10 μm fraction of high acid leach residue (#8298). The sample consists of discrete crystals, ∿10 μm in size, as well as masses of granular material (upper left) in which the individual particle sizes are <1 μm.

Figure 3 illustrates the same material but at a higher magnification. The grey blocky crystals are jarosite which contains Pb, Zn, Cu, Al, Si and K. Sodium was not conclusively identified in the jarosite, but this element is not readily detected by SEM-EDX. Both Pb and K were detected in all the jarosite grains and discrete crystals of either lead jarosite or alkali jarosite were not seen. There is a suggestion that the coarser grains contain less Pb than the granular jarosite, but the latter is much too fine to permit quantitative electron microprobe analysis. Since the X-ray powder diffraction analysis revealed two jarosites, however, it may well be that the jarosite grains are extensively zoned as has been observed in natural crystals (2). The small white grains in the photograph (Figure 3) are generally zinc ferrite crystals although occasional grains of barite ($BaSO_4$) and cassiterite (SnO_2) also were observed. Barium was commonly detected as a trace constituent in the jarosite grains, and this is assumed to be due to fine inclusions of $BaSO_4$ in the jarosite and not to the substitution of Ba in the jarosite structure. Trace indium was also detected, and this element likely substitutes for iron in the jarosite structure. Occasional grains of quartz and Ca-Mg-Fe oxides (large dark grey grain at left of photo) were also detected. The finely granular crystal masses (upper left, lower center) consist almost entirely of jarosite containing Pb, Zn, Cu, K and traces of Si and Al.

Figure 4 illustrates the -10 μm high acid leach residue in more detail. All the larger, grey platy crystals are jarosite with detectable Pb, Zn,

Cu, K and traces of Al and In. The white grain (upper right) is SnO_2, and the other white to light grey grains are zinc ferrite. The extremely small size of the individual crystals in the granular part of the sample is evident; individual crystals <1 μm are common. Again, SEM-EDX analysis of the fine crystals showed them to be basically the same as the coarser jarosite grains.

X-ray mapping of the -10 μm fraction of the high acid leach residue richest in silver failed to detect any concentrations of silver, thus suggesting that this element is more or less evenly distributed throughout the sample. Silver was not detected in any of the grains examined by SEM-EDX, but this technique is not overly sensitive for silver (detection limit ∿5000 ppm Ag). The jarosite grains were also examined by the electron microprobe since this can detect lower levels of silver than the SEM-EDX system. Although the fine size of the jarosite particles made a strictly quantitative analysis impossible (the beam always overlapped some of the mounting medium and/or other phases), the electron microprobe clearly showed that the silver was associated, at least in part, with the jarosite grains. For example, a typical analysis yielded: Fe 16.94%, Pb 9.89%, S 11.40% and Ag 500 ppm. Presumably, analysis of just the lead jarosite grains (where Pb ∿18% and Fe ∿29%) would result in still higher Ag levels (∿900 ppm Ag?). Given that jarosite-type compounds constitute the bulk of the sample (Figure 2) and that the jarosite seems to contain high silver values, it is concluded that the jarosite phase carries much of the silver in the residues.

CONCLUSIONS

Both the neutral leach residue and the high acid leach residue produced by Kidd Creek Mines Limited, Timmins, Ontario contain jarosite-type compounds. Although SEM-EDX analysis suggested the presence of a single jarosite containing Pb, K, Zn, Cu, Al and lesser amounts of Si and In (Na not readily detectable), X-ray powder diffraction analysis indicated the presence of both lead jarosite and an alkali jarosite (likely Na-K-jarosite). The individual jarosite grains are generally <10 μm and are commonly <1 μm. Electron microprobe analysis indicated that the silver is associated, at least in part, with the jarosite phases, but the fine size of the jarosite grains and the low silver concentration prevented the quantitative measurement of the amount of silver.

ACKNOWLEDGEMENTS

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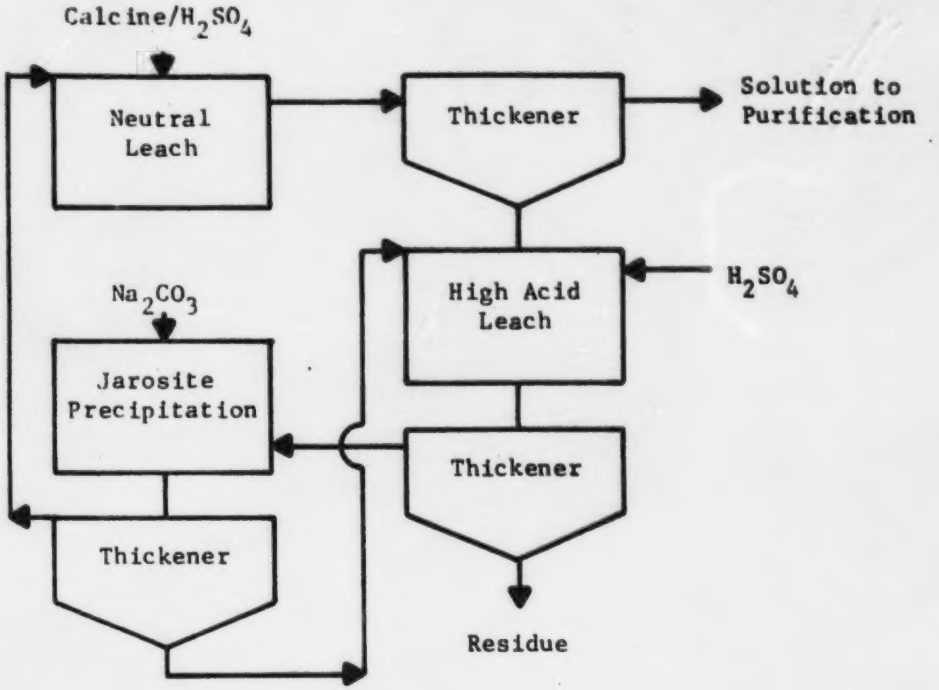
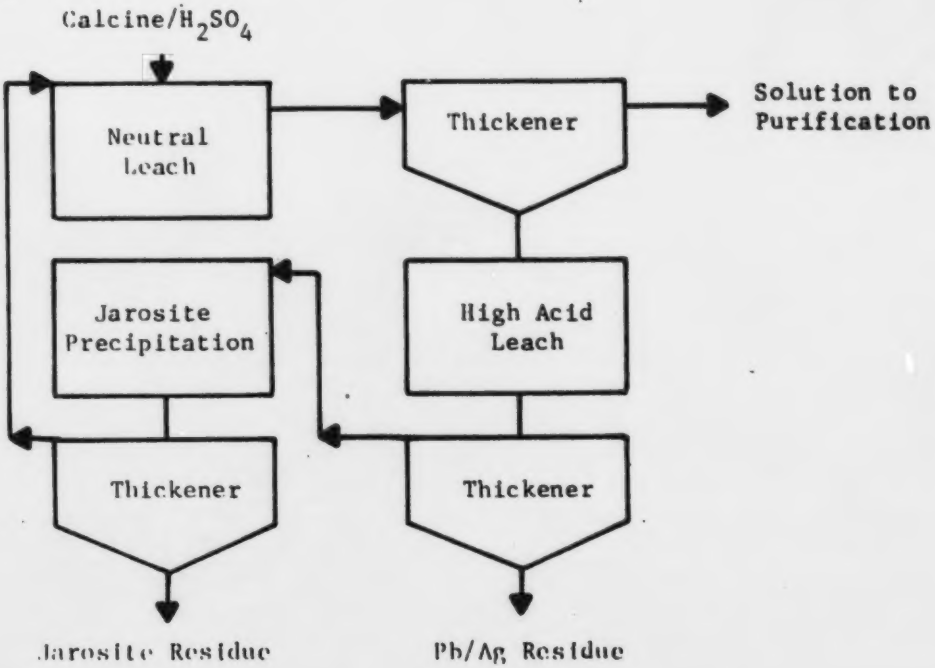


a) One-residue option



b) Two-residue option

Fig. 1 - Comparison of the one-residue and two-residue flowsheets.

Fig. 2 - General view of the -10 μm fraction of the high acid leach residue. (SEM secondary electron micrograph.)

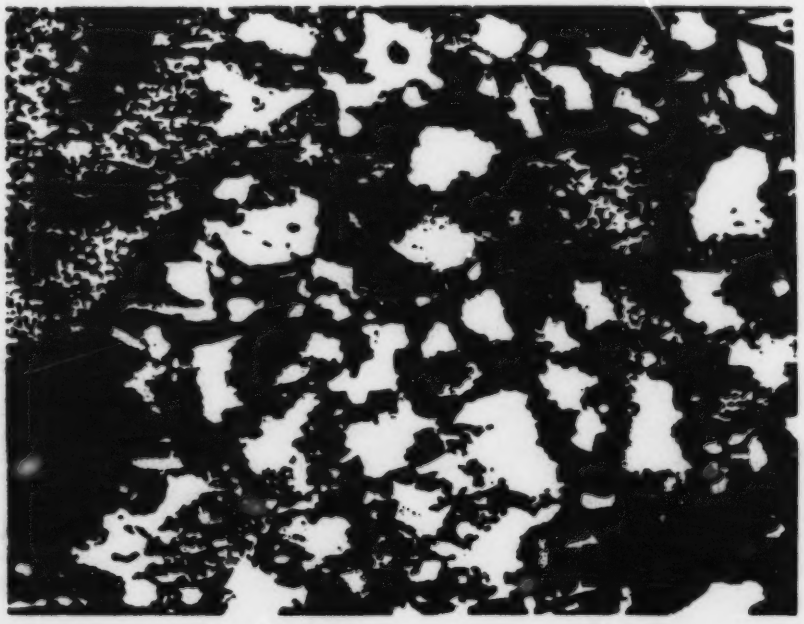


Fig. 3 - Detailed view of the -10 μm fraction of the high acid leach residue showing some of the coarser particles as well as the granular material. (SEM secondary electron micrograph.)

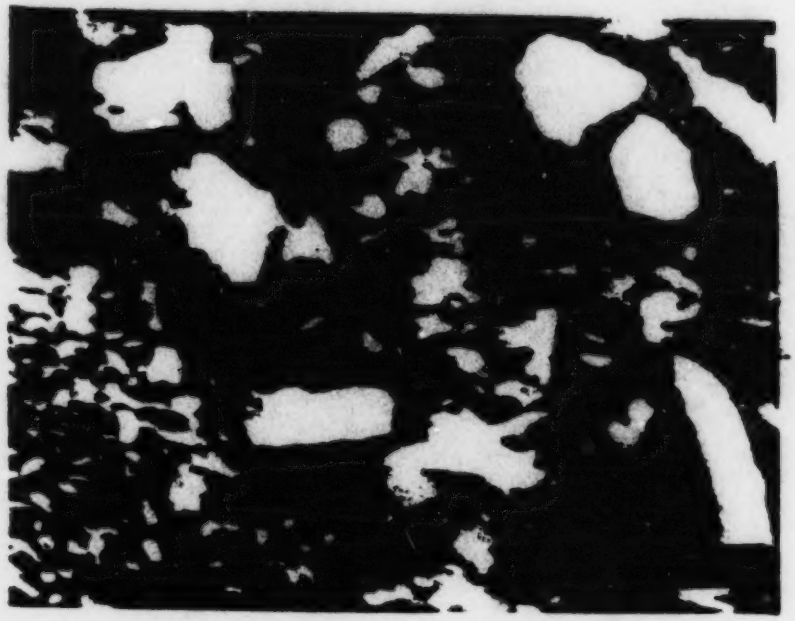


Fig. 4 - High resolution view of the coarse and granular jarosites present in the -10 μm fraction of the high acid leach residue. (SEM secondary electron micrograph.)